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In-situ transesterification of rapeseed and cost indicators for biodiesel production

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ABSTRACT

In the present work the alkali in-situ transesterification of rapeseed with methanol for the production of biodiesel fuel was studied. Experiments were designed to determine how variations in molar ratio of methanol to oil in seeds, amount of alkali catalyst, time and temperature affected the yield. Good results (90%) conversion of seed lipid to fatty acid methyl ester was obtained at 0.02 N catalyst concentration, 720/1 methanol to rapeseed oil molar ratio, 1 h reaction time and 65 °C reaction temperature. The results were in agreement with the values measured by ^{1}H NMR spectroscopy. A mass balance and a preliminary feasibility study were investigated. A techno-economic analysis of the process for production of biodiesel from rapeseed with a capacity of 50,000 t/yr was presented to investigate the profitability indicators of the production capacity. The techno-economic indicators showed that total capital investment of $16,065,000, gross profit/year of $14,630,300, and percentage simple rate of return (%SRR) was 79.5% for a constant estimated price of $945/t while the specific biodiesel prices for SRR% of 10 and 50 were $722 and $850 respectively.

Contents

1. Introduction

Biodiesel is a renewable fuel [1] produced by transesterification of vegetable oils using an alcohol and a catalyst [2,3]. The transesterification reaction can be catalyzed by acidic [4], alkali [5–7], or enzymes [8–12]. The process usually uses pre-extracted oil as raw material, which is usually produced by mechanical pressing followed by solvent extraction to extract any remaining oil. Alternatively, biodiesel can be produced via 'in-situ transesterification' or 'reactive extraction' [13–16]. This process combines the steps of lipid (oil) extraction and transesterification to produce biodiesel. Integration of these stages could reduce

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biodiesel production cost [16–18]. The use of reagents and solvents is reduced, the analysis is less expensive and easier, and the concern about waste disposal is avoided. The main concerns in performing in-situ reactions are lipid solubilization (advisable to achieve fast and complete reaction) and prevention of the interference of water or other compounds. Many parameters play important roles in optimizing the process [19] such as reaction temperature, time, molar ratio of alcohol to oil and catalyst concentration. The steps and parameters involved in the integrated extraction/reaction scheme differ from that of the conventional process in many ways due to the dependence on both extraction and reaction. Zakaria [20] illustrates that the parametric studies and light microscope images of reactively extracted seed suggested that reactive extraction occurs by transesterification of the oil inside the seed, followed by diffusion of the products into the bulk solvent.

Many researchers investigated the in-situ approach for biodiesel production [21,22]. Georgogianni et al. compared alkaline in-situ Transesterification of both sunflower seed oil [22] and cotton seed oil [23] with conventional transesterification. The authors found that in-situ transesterification gave similar ester yields to those obtained by conventional transesterification. Also Harrington and D'Arcy Evans [17] showed that transesterification of sunflower seed oil in-situ with acidified methanol produce fatty acid methyl esters in yields significantly 20% greater than those obtained from conventional reaction. Haas et al. examined alkaline in-situ transesterification of soybean flakes [16] and from a variety of feed stocks [24]. Madankar et al. [25] studied the production of castor oil methyl ester by reactive extraction, and found that the optimum reaction conditions were 1% KOH (wt. basis of oil) reaction temperature 65 °C, reaction time 3 h, methanol to oil molar ratio 250:1 and mixing speed of 600 rpm. The authors concluded that in-situ approach might be valid for the production of biodiesel from virtually any lipid-bearing material. Similarly, high conversion of lipid to fatty acid methyl ester has been reported in rice bran [19], canola [21], castor seed oil [26], cotton seed oil [27], *Jatropha curcas* L. seeds [28] and rape seed oil [29]. Fan et al. [30] gave a preliminary study of two approaches to economically produce biodiesel from waste cooking oil and flaked cottonseed. One was to use the ultrasound-assisted synthesis of biodiesel from waste cooking oil and the other was the application of in-situ transesterification from flaked cottonseed.

The main objective of the present work was to apply the biodiesel production technology using an alkaline catalyst to the in-situ transesterification of rape seed and to study the effect of time, temperature, catalyst concentration, and methanol: seed ratio. As a means for the cross-checking results analytical method, the ^{1}H NMR method was selected. Since the quantification method by NMR was discussed in previous publication [31], no further discussion will be presented here. The second objective was to present a mass balance for an industrial scale production based on experimental data and to develop an economic study to produce 50,000 t biodiesel/year.

2. Experimental work

2.1. Materials

- Rapeseeds used were supplied by Cultivation and Production of Medicinal and Aromatic Plant Dept. at National Research Centre of Egypt. From our previous work [32], the percentage of oil in rapeseeds was found to be 38%, and moisture content of seed is around 6%. Table 1 illustrates the comparison between the fatty acid composition of rapeseed oil used and data found in literature.
- Methanol of 99.8% analytical reagent.
- Potassium hydroxide pellets of 98% purity as catalyst.
- Glacial acetic acid analytical grade to stop the reaction.

Table 1
Fatty acid composition of rapeseed oil.

Constituent	% Composition from the present work [32]	% Composition from data in literature [33–54]	
		Mean	Dev.
Palmitic (16:0)	4.39	4.2	1.1
Stearic (18:0)	1.67	1.6	0.7
Oleic (18:1)	60.95	59.5	7.8
Linoleic (18:2)	19.04	21.5	2.8
Linolenic (18:3)	11.78	8.4	1.3
Eicosic (20:1)	2.7	2.1	3.0
Erucic (22:1)	0.9	0.5	0.5

- Carbon tetrachloride analytical reagent to extract the produced biodiesel from reaction mixture.

As shown from Table 1 there is slight deviation in composition. Erucic acid is much higher in the present study it is more favorable to be used as fuel.

2.2. Procedure

Reactive extraction experiments were carried out according to the following experimental procedure:

1. Whole seeds (40 g) were macerated in methanol (100 ml) and a laboratory homogenizer (1800 rpm) was used for 1 min to give slurry with particle size of coarse sand.
2. The slurry was transferred to the reaction flask and methanol was added to achieve the required pre-determined molar ratio and is heated under reflux.
3. The relevant amounts of catalyst (KOH) was dissolved in 50 ml methanol using magnetic stirrer/hot plate. When the catalyst was completed dissolved, it was added to the reaction flask after the mixture reached set temperature and the reaction time started.
4. To ensure that the transesterification reaction is stopped, the catalyst was neutralized using glacial acetic acid.
5. The reaction mixture was filtered to separate the meal and the liquid mixture.
6. The liquid mixture was placed in a rotary-evaporator to evaporate the methanol. Then carbon tetrachloride was added to the solution and transferred to a separating funnel and was allowed to separate. Two distinct layers, the biodiesel-carbon tetrachloride lower layer, and the glycerol-rich upper layer appeared.
7. The lower layer was then placed in the rotary-evaporator to remove carbon tetrachloride to obtain pure biodiesel.

All experiments were duplicated. The reactive extraction was studied for different concentrations of KOH, mole ratio, reaction temperature and time intervals. NMR spectra were obtained on a JEOL ECA at 500 MHz, using $CDCl_3$ as a solvent.

3. Results and discussion

The percentage yield conversion of biodiesel was calculated based on the total amount of oil in the seed, concerning experimental and analytical error to be ± 2%.

3.1. Effect of catalyst concentration:

The effect of catalyst concentration after 90 min reaction, 65 °C temperature and methanol:oil molar ratio 720:1 is shown in Fig. 1.

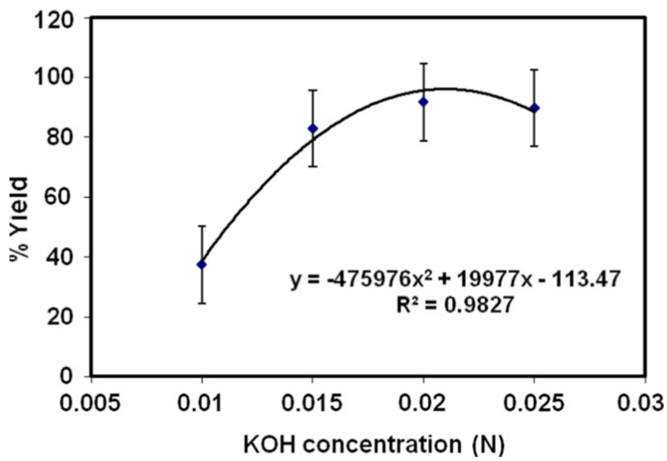


Fig. 1. Effect of catalyst concentration on methyl ester yield (alcohol to oil 720:1,reaction time 90 min, reaction temperature 65 °C).

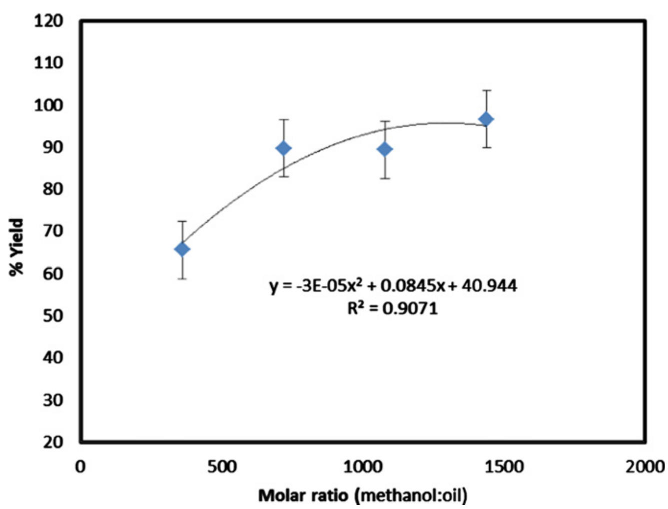


Fig. 2. Effect of molar ratio of alcohol to oil on methyl ester yield (catalyst concentration.0.02 N, reaction time 90 min, reaction temperature 65 °C).

The graph clearly shows that the yield of biodiesel increases with increase in the concentration of catalyst. Without addition of KOH in methanol, the in-situ alkaline transesterification almost did not occur. This can be explained that methanol itself is a poor vegetable-oil extractor, so alkaline alcohol destroys intracellular compartmentalization in the seeds, allowing solubilization and subsequent transesterification and that agree with Ren et al. and Kasim and Harvey [29,55]. The yield of biodiesel at 0.02 N KOH was found to be 90%; while at 0.025 N KOH the yield was found to be 89%. It is known that further increase in KOH concentration increases the amount of soaps formed by saponification reaction [54]. The soap increases the methyl ester solubility in glycerol and produce emulsification of the ester and glycerol that makes difficulties in the separation of the esters. Therefore the ester losses increase and consequently the yield decreases. These results agree with Zakaria [20] who found that increasing the catalyst concentration from 0.1 to 0.15 M NaOH causes a reduction in the yield in case reactive extraction of rapeseed oil.

3.2. Effect of molar ratio of methanol to rapeseed oil

The methanol volume required in reactive extraction is very high compared to the conventional process [16]. In this study, the molar ratio of methanol to rapeseed oil was varied from 360 to 1440; other conditions are shown in Fig. 2. As shown in this figure, by increasing the amount of loading methanol, rapeseed oil extraction and conversion were increased considerably. When the methanol:oil molar ratio was very close to 720:1, the amount of yield reached 90%. However, beyond the molar ratio 720:1 the excessively added methanol had slight effect on rapeseed oil extraction and conversion. The yield at a molar ratio of 1080 is 89% and the yield at 1440 is 96% from the total amount of oil in seeds. The results suggested that the amount of methanol must be very high to achieve an appreciable rate. This was presumably to drive the penetration of alkaline methanol into the seed [23]. Further excess of methanol is undesired, as it will increase the load on downstream separation processes, this fact is in accordance with Kasim et al. [55] for in-situ transesterification from castor seeds. For economic reasons, the ratio of 720:1 is selected as an optimum.

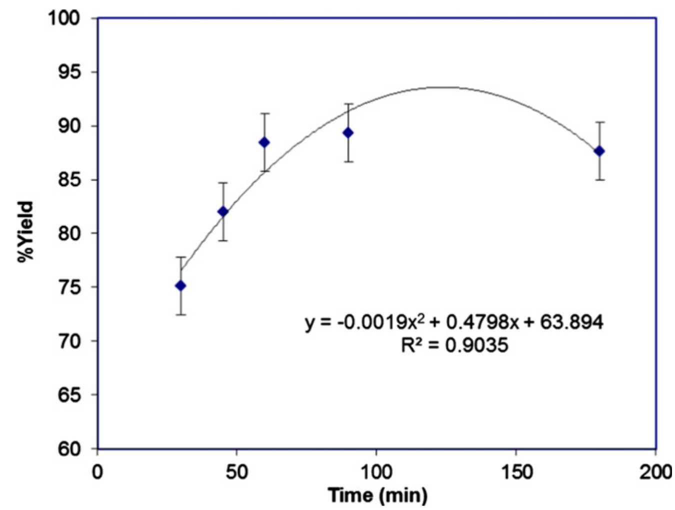


Fig. 3. Effect of reaction time on methyl ester yield (alcohol to oil 720:1, catalyst concenration 0.02 N, reaction temperature 65 °C).

3.3. Effect of time

The reaction rate of plant oil seeds reactive extraction has been claimed to be very high [16].

The results obtained from experiments are presented in Fig. 3. Reaction was carried out for three hours; other conditions are shown in the figure. The yield was increased with the increase of reaction time. Within one hour about 90% yield was obtained for biodiesel production and further increase in the reaction time from 1 to 3 h had no effect on the biodiesel yield.

3.4. Effect of temperature

Two reaction temperatures were investigated, 65 °C which suffices to achieve rapid reaction (boiling point of the system) and 30–35 °C (room temperature) at which heating of the reaction is not required and at which the reduced volatility of the alcohol component reduced vapor entrainment and reduced the need for solvent replacement. The data obtained are plotted in Fig. 4. Percentage yield at 35 and 65 °C was 83 and 90, respectively. Temperature did not have a significant effect on biodiesel yield. This result is in agreement with the work by Haas et al., where they observed that triglyceride can be converted to biodiesel at both low and high temperature [16]. Karnwal et al. found that ester yield from Thumba oil decreases as the reaction temperature increases above 60 °C [56]. Atapour and Kariminia [57] said that yield of biodiesel from Iranian bitter almond oil

increased when the reaction temperature was raised from 30 to 50 °C then further increase in temperature (from 50 to 70 °C) caused a decrease in the yield. Several researchers found that the increase in temperature influences the reaction in positive manner [58–60].

4. The proton NMR spectrum

The characteristic signals in the ^{1}H NMR spectrum illustrate that the strong singlet at 3.7 ppm for integration of methoxy groups in the methyl esters ($-CO_2CH_3$) and the triplet signal at 2.3 ppm indicates α-carbonyl methylene groups ($-CH_2CO_2CH_3$) present in all fatty ester derivatives. No visible glycerol related signals were found at 4.1–4.4 ppm. The results were in agreement with the values measured by ^{1}H NMR Spectroscopy [61,62].

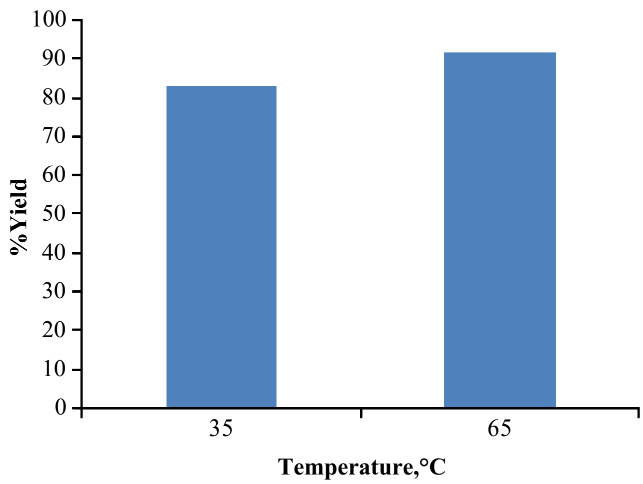


Fig. 4. Effect of temperature on methyl ester yield. (Catalyst concentration 0.02 N, reaction time 90 min, alcohol to oil 720:1.)

5. Physical/chemical properties of biodiesel (FAME) from rapeseed oil

Table 2 summarizes several of the most important physical/chemical properties of biodiesel (FAME) derived from rapeseed feedstock whose composition profile was discussed in Table 1.

6. Mass balance

A mass balance for pilot scale of 1.0 t biodiesel production from rapeseeds by the in-situ transesterification process was achieved using optimum reaction conditions for the best yield of 90% and demonstrated in Fig. 5. The optimum conditions from experimental work were 0.02 N catalyst concentration, 720/1 methanol to rapeseed oil molar ratio, 1 h reaction time and 65 °C reaction temperature. As shown from Fig. 5 1 t produced biodiesel needs 2.85 t seeds which contain 38% oil.

Table 3
Annual products and by-products sell cost.

Name of material	Price ($/t)	Annual amount (t/yr)	Annual value of product ($/yr)
Biodiesel	945	50,000	47,250,000
Cake	133	68,000	9,044,000
Glycerol	200	5,000	1,000,000
Total annual value of products			**57,294,000**

Table 2
Physical/chemical properties of biodiesel (FAME) derived from rapeseed feedstock.

Property	Rapeseed from present work	Rapeseed from literature [63]		ASTM
		Mean	Dev.	
Cloud point (°C)	−3	−3	2	Report customer ASTM D2500
Pour point (°C)	−6	−10	3	−15 to10 ASTM D79
Flash point (°C)	163	169	16	> 130 ASTM D93
Cetane no.	48	53.7	2.9	47 min ASTM D613
Specific gravity	0.8848	0.879	0.01	0.87–0.9 ASTM D1298
Higher heating value (MJ/kg)	40.08	41.1	2.3	ASTM D224
Sulfur content (ppm)	Nil	4	3	15 ASTM D4294

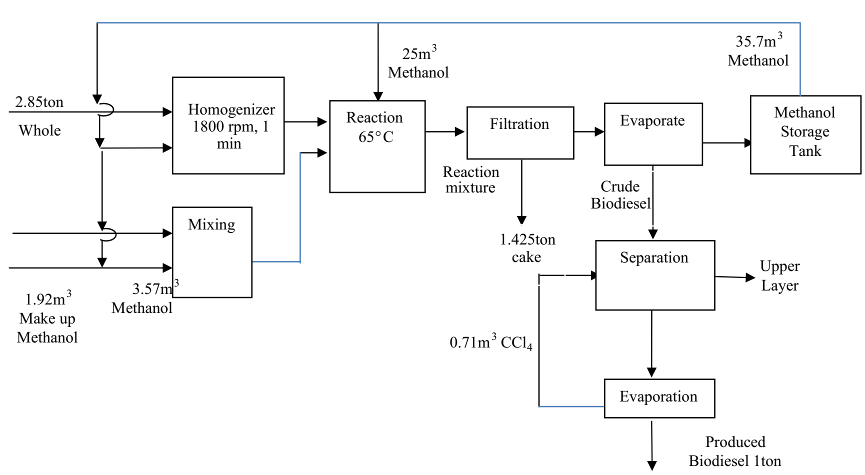


Fig. 5. Pilot scale mass balance flow chart for in-situ transesterification of 1 t biodiesel production from rapeseeds.

7. Techno-economic cost analysis

Based on experimental work on bench and pilot plant, optimum operating conditions for biodiesel production have been investigated, mass and energy balance outputs from the production of 1.0 t. Biodiesel pilot scale shown in Fig. 5 were used to evaluate all capital and operating costs in order to establish an overall cost of production value. Glycerol and protein-meal for livestock feeding are by-products that might help to offset the cost of production. The economical evaluations were carried out for a continuous biodiesel production plant. The cost evaluation of this study were based on the following assumptions; the plant capacity of biodiesel production was 50,000 t/yr, rape seed (250$/t) used as the feedstock for biodiesel production, was free of any solid impurities. Operating hours based on three shifts (8 h) per day and 300 working days per year (7200 h/yr). The storage capacity is 2 weeks for raw materials and 3 weeks for products. The installation cost was estimated based on 400% on equipment cost. Depreciation estimated using the straight line method and assuming life span of 10 yr. From an economic point of view, in-situ alkaline transesterification requires a higher methanol to oil ratio, the cost of methanol recovery accounts for a part of the cost of biodiesel production. Therefore, in order to reduce methanol consumption and increase efficiency, reaction methanol recycling is of great importance for industrial application. Qian et al. [27] showed that the optimum methanol recycling ratio of the in-situ alkaline transesterification was 0.2.Annual products and by-products sell cost are shown in Table 3. Equipment size based on the mass production and cost estimation of the process equipment has been estimated from McGraw Hill [64] and prices have been adjusted based on cost indices of 2011 as presented in Table 4. All chemical costs, total utilities cost for superheated, low- and high-pressure steams, electricity and water and annual operating labor costs are shown in Tables 5 and 6. The techno-economic analysis indicators for the in-situ and conventional method [65] are shown in Table 7. The gross profit is found to be $14,630,300 for the in-situ and $8,176,830 for the conventional method, which correspond to %SRR given as 79.5% and 29.4, respectively, for constant estimated prices of $945/t. It is to be noted that the specific biodiesel prices, if SRR% are 10 and 50, are estimated to be $722 and $850 respectively for the in-situ process.

8. Conclusions

In-situ transesterification has now been demonstrated to be an effective method for fatty acid methyl ester production from rapeseed rather than the conventional method. This study was designed to determine the effect of various parameters on the reactive extraction of rapeseed. Effects of methanol to oil molar ratio, potassium

Table 4
Equipment cost.

Storage facilities	No. of units	Price ($)
Seed storage tank	1	550,000
Biodiesel storage tank	1	500,000
CCL_4 storage tank	1	30,000
Crude glycerol storage tank	1	33,000
Loading/unloading stations	1	75,000
Pumps to/from storage	5	33,000
Subtotal storage facilities		**1,221,000**
Process equipment		
Methanol storage tank	1	36,000
Potassium hydroxide tank	1	37,500
Homogenizer	1	10,500
Reactor	2	225,000
Glycerol biodiesel separator (Filter press)	1	466,500
Methanol distillation tower	1	180,000
Biodiese4l/CCl4 evaporator	1	50,000
Fatty acid storage tank	1	15,000
Pumps	12	93,000
Additional process equipment	1	649,500
Subtotal processing		**1,763,000**
Utility equipment		
Steam generation system	1	104,000
Instrument air system		25,000
Electrical distribution system		100,000
Subtotal utility equipment		**229,000**
Total equipment cost		**3,213,000**
Other costs		
Installation, @ 400% of equipment costs		12,852,000
Total other costs		**12,852,000**
Total costs		**16,065,000**
Depreciation based on 15 yr life span		**1,071,000**

Table 6
Annual operating labor costs.

Labor	Number of operators per shift	Shifts per day	Operator rate (\$/h)	Annual operating labor cost (\$/yr)
Engineer	2	3	5	72,000
Supervisors	2	3	3	43,200
Administration	5	3	2	72,000
Laborer	5	3	2	72,000
Total				259,200

Table 7
Techno-economic indicators.

	Conventional	in-situ
Total annual cost of raw materials	$52,359,841	$42,099,750
Annual operating labor costs	$259,200	$259,200
Total utility Cost	$521,000	$521,000
Total equipment cost	$4,105,550	$16,065,000
Depreciation @10% capital cost/year	$1,368,516.667	$1,071,000
Total production cost/year	$54,508,557	$43,950,950
Total annual value of products	$62,685,387.500	$58,581,250
Gross profit/year	$8,176,830	$14,630,300
%SRR	29.4	79.5
Pay pack period, month	30.1	13.2

Table 5
Utility cost.

Utility	Default unit cost	Default cost units	Annual utility requirement, in appropriate units	Default units of utility requirement	Annual utility cost (\$/yr)	Annual utility cost (LE/yr)
Electricity	0.030	$/kWh	2,700,000	kWh/yr	81,000	486,000
Steam, saturated, 790 kPa	6.00	$/1000 kg	40,000	1000 kg/yr	240,000	1,440,000
Process water	0.08	$/m^3$	2,500,000	m^3/yr	200,000	1,200,000
Total utility cost					521,000	3,126,000

hydroxide concentration, reaction temperature and reaction time on the yield were studied. The results indicated that these parameters were important factors affecting the yield. A high biodiesel yield of 90% was achieved at 0.02 N catalyst concentration, 720/1 methanol to rapeseed oil molar ratio, 1 h reaction time and 65 °C reaction temperature. Mass balance to produce 1.0 t of biodiesel is developed and based on which a preliminary economic study to produce 50,000 t/yr of biodiesel is achieved and showed promising results. The techno-economic indicators shows that total capital investment of $16,065,000, gross profit/year of $14,630,300, percentage simple rate of return (%SRR) was 79.5% for a constant estimated price of $945/t while the specific biodiesel prices for SRR% of 10 and 50 were $722 and $850 respectively.

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